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CLASS REACTIONS AND IDENTIFICATION

OF

ORGANIC SUBSTANCES

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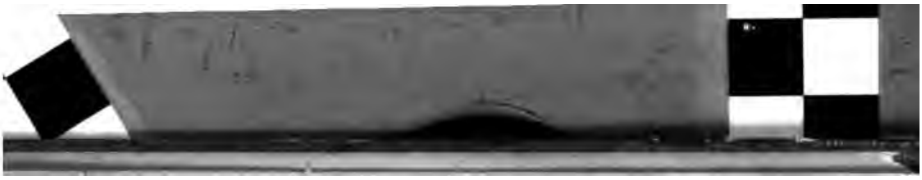

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ORGANIC SUBSTANCES.

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PREFACE.

THIS collection of laboratory experiments in organic chemistry has been prepared especially for the use of the classes of the Massachusetts Institute of Technology, as a supplement to the ordinary course of instruction in preparation work. The authors' experience has shown that the preparation of typical organic substances in accordance with the plans followed in the manuals of Gattermann, Levy, Fischer, etc., teaches satisfactorily the manipulative methods of organic chemistry and the manner of execution of the leading synthetic processes, but that it fails, to a surprising extent in the case of most students, to give a knowledge of the important characteristics of the various classes of organic compounds, and therefore of the fundamental principles of the science. Unless the instructor is continually on the alert, the course of preparation work becomes almost unavoidably a routine following of directions.

Although the primary purpose of the experiments here described is to illustrate the characteristic reactions of organic compounds, their analytical significance is a feature of no slight importance; for, both in research and technical work, the chemist has frequent occasion to identify the substances he meets with. On this account, and also because it is always desirable to make evident to the student some practical use of the information presented to him, the analytical side of the experiments has been made prominent; and an important part of the course consists in the identification of unknown compounds and the quantitative separation of mixtures by methods devised by the student himself with the help of the knowledge gained from the experiments with known substances.

It is believed that the entire omission of explanatory statements of what occurs in the experiments will cultivate the student's power of observation, and cause him to consider more carefully the principle illustrated; while the work on the identification and separation of unknown substances will afford abundant opportunity for original thought. — It is assumed that a brief course of lectures on the outlines of organic chemistry has preceded the laboratory experiments.

Owing to the great importance, in the opinion of the authors, of instruction of this kind, and owing to the fact that no text-book presenting it exists, it has not seemed advisable to postpone the publication of the general plan, although it is undoubtedly imperfect in many matters of detail.

The authors desire to express their indebtedness to Dr. J. F. Norris for many valuable suggestions, and to Messrs. H. M. Loomis, A. P. Norris, and C. L. W. Pettee, for their investigations on the applicability of many of the important tests.

PART I.

EXPERIMENTS ILLUSTRATING THE CLASS REACTIONS OF ORGANIC COMPOUNDS.

Introductory Explanations and Directions.

THE following experiments serve to illustrate some of the most important properties and reactions of the various classes of organic compounds. The results obtained are to be regarded as characteristic of the whole class as defined by the heading above the experiment. It must, however, be clearly understood that all compounds of the class do not give these reactions with equal facility — that, indeed, complex members of the class, and especially those belonging at the same time to two or more classes, often do not give them at all. Moreover, many of the reactions are general for more than one class; but, when this is true, it will be pointed out, as far as practicable, in the notes following the experiments.

Statements of what occurs are omitted from the following directions; and the student is expected to observe carefully and record fully in the note-book everything that happens, even those things of apparently minor importance. Attention should be directed not only to what may be seen, but also to any odor or to any heat effect developed. The observed phenomena should then be fully explained with reference to the new compounds formed; and all the reactions where known products are formed should be written,

using structural formulæ. Works on organic chemistry should be consulted when necessary. The notes following the experiments must be very carefully studied.

After completing the experiments, make a table in the note-book showing, as far as possible, the behavior of each class of compounds towards each of the following reagents: cold dilute alkaline hydroxides; boiling concentrated alkaline hydroxides; concentrated sulphuric acid alone and with subsequent addition of water; sodium; and bromine water.

Students are warned that many of the reactions may take place suddenly and with great violence, and that, therefore, cautious manipulation is necessary, particularly in test-tube experiments.

Behavior of Organic Substances on Ignition.

1. Ignite in a small crucible, as long as any change occurs, first a little benzoic acid, and then a little starch.

Repeat the experiment with a little anhydrous sodium acetate. Add a drop of dilute hydrochloric acid to the residue after cooling.

This reaction with hydrochloric acid is given only by organic salts of the alkalies and alkaline earths.

Detection of Water in Organic Liquids.

2. Add 0.2 gram of fused pulverized potassium carbonate to 5 cc. of common 95 per cent. alcohol. Shake and set aside for an hour.

Repeat this experiment, using 5 cc. of the same alcohol diluted with 1 cc. of water.

3. Add 0.5 gram copper sulphate, freshly dehydrated by ignition at a low temperature, to 5 cc. of

ordinary 95 per cent. alcohol. Shake and allow the mixture to stand for about one hour.

Reactions Distinguishing Double and Triple-Bonded from Single-Bonded Compounds.

4*a*. Dissolve 0.5 gram of amylene in 5 cc. of carbon tetrachloride, and add gradually a 10 per cent. solution of bromine in carbon tetrachloride as long as any action occurs.

Repeat this experiment, using first cinnamic acid, then phenol, and finally toluene, in place of the amylene. In the cases of the cinnamic acid and toluene, after allowing the mixture to stand in the cold for two or three minutes, heat it to boiling for about a minute.

Decolorization without evolution of hydrobromic acid shows *addition*, and therefore the probable presence of a double or triple bond. Decolorization accompanied by evolution of hydrobromic acid shows *substitution;* but it does not necessarily exclude the possibility of a simultaneous addition, which may even be inferred in case the evolution of hydrobromic acid is not proportionate to the rate of decolorization. If even on heating no action occurs, or if only a slow action accompanied by evolution of hydrobromic acid takes place, it is probable that no double or triple bond is present; it is true, nevertheless, that there are some double-bonded compounds (for example, fumaric, maleic, and the nitro-cinnamic acids) which form addition-products only very slowly or not at all under the conditions of this experiment. On the other hand, amines, phenols, and most aldehydes and ketones, like double-bonded compounds, decolorize the bromine solution instantly; in the case of amines, often without evolution of hydrobromic acid.

4*b*. Dissolve 0.5 cc. of allyl alcohol in 5 cc. of water, and gradually add bromine water as long as decolorization takes place.

Repeat the experiment, using ethyl alcohol instead of allyl alcohol.

As bromine water is used as a reagent in other cases, this experiment is introduced here, in order to show its behavior with unsaturated compounds. But, as a means of distinguishing them from saturated bodies, the test in carbon tetrachloride is far more satisfactory: for, when water is used as the solvent, any hydrobromic acid formed is absorbed by it, so that it is not readily possible to distinguish substitution from addition; moreover, besides these two actions, oxidation often takes place in aqueous solution; and finally, the unsaturated compounds which fail to react in carbon tetrachloride are almost equally inert in water, so that the latter solvent has no advantage in this respect.

5. Add 0.2 gram of cinnamic acid to 5 cc. of sodium carbonate solution, and then add drop by drop about 1 cc. of a one per cent. solution of potassium permanganate.

Repeat the experiment, using first amylene and then toluene in place of the cinnamic acid.

The oxidation takes place almost instantaneously with unsaturated compounds, and with some saturated ones, such as formic acid, malonic ether, phenols, oxybenzoic acids, benzaldehyde, acetone, acetophenone, glycerine, and some sugars. But most saturated compounds are oxidized much more slowly, if at all.

Reactions of Triple-Bonded Compounds Containing the ($\equiv C - H$) Group.

6. Add 1 cc. of ammoniacal cuprous chloride solution to 10 cc. of a saturated aqueous solution of acetylene and shake.

Behavior Distinguishing Saturated Fatty Compounds Containing No Complex Alkyl Radicals from Other Compounds.

7. Roll a piece of fine copper gauze 1 cm. square around the end of a copper wire. Dip this in succes-

sion into small tubes containing (*a*) toluene, (*b*) benzoic acid, (*c*) allyl alcohol, (*d*) sugar, (*e*) ethyl ether, and (*f*) amyl alcohol. (In the case of the solid substances, take care to make a considerable amount adhere to the gauze.) Hold the substance in a gas flame until it takes fire; then remove it, and note whether soot is produced, holding a piece of white paper behind the burning substance.

Almost all aromatic compounds, hydrocarbons, unsaturated fatty compounds, and fatty compounds containing alkyl radicals with four or more carbon atoms, when they can be burnt as here described, produce soot in considerable quantity. Other fatty compounds under the same conditions produce, as a rule, no soot.

Behavior of Hydrocarbons in General.

8. Add 1 cc. of toluene first to 5 cc. of water, and then to 5 cc. of dilute sodium hydroxide solution (1 : 10), and shake.

Many *solid* aromatic hydrocarbons are heavier than water.

9. Add a thin slice of sodium to a few cubic centimeters of toluene in a perfectly dry test-tube.

In the case of solid substances or in case only a slight effervescence occurs, the test should be made as illustrated by the following experiment.

10. Fill a small test-tube completely with anhydrous alcohol-free ether; drop to the bottom a thin slice of bright sodium (3 cm. long, 1 cm. wide); and insert at once a clean, dry rubber stopper, through which passes a small glass tube which reaches nearly to the bottom of the test-tube and is there turned upwards for a distance of a few millimeters, and which is bent above the stopper so as to deliver into another test-tube. Allow the action to continue

for fifteen minutes, and make a mark on the tube to show the amount of gas produced.

Dissolve 1 gram of naphthalene in a test-tube full of the same ether, and repeat the above experiment.

The ether for this experiment will be found in the laboratory. It is prepared by washing commercial ether eight or ten times with small quantities of strong salt solution, drying it for at least one day over a large quantity of calcium chloride, treating through several days with successive portions of sodium, and finally distilling over sodium with every precaution to avoid access of moisture. The product should be kept over sodium in a bottle provided with a drying tube.

Reactions Distinguishing Hydrocarbons of the Methane (C_nH_{2n+2}) from Those of the Benzene (C_nH_{2n-6}) Series.

11. Thoroughly mix together by shaking in a wide test-tube 2 cc. of petroleum ether and 5 to 6 cc. of fuming sulphuric acid (sp. gr. 1.89 at 20°). Pour the mixture very slowly and cautiously into three volumes of cold water, and allow it to stand a few minutes.

Repeat this experiment, using toluene instead of petroleum ether.

12. Repeat both parts of Experiment 11, using fuming nitric acid (sp. gr. 1.48) in place of sulphuric acid. As the action may suddenly become very violent, great care must be taken to hold the tube in such a position that its contents cannot be thrown out upon the experimenter.

In the case of entirely unknown substances, very small quantities should first be experimented with.

Behavior of Halogen-Substituted Hydrocarbons.

13. Add 1 cc. of ethyl bromide first to 5 cc. of water, and then to 5 cc. of dilute sodium hydroxide solution, and shake.

The monochlorinated derivatives of the fatty hydrocarbons are lighter than water.

Reactions Distinguishing Halogen Compounds of Different Types.

14. Add three drops of ethyl bromide to 5 cc. of an alcoholic solution of potassium hydroxide (free from chlorine), and boil gently for two minutes. Dilute with water, acidify with nitric acid, and add a few drops of silver nitrate solution.

Repeat this experiment, using first benzyl chloride, and then brombenzene in place of the ethyl bromide.

In experimenting with unknown substances, in order to make sure that they contain no free halogen or halogen acid, it is advisable to wash them with dilute sodium carbonate solution before applying the test.

The behavior of ethyl bromide is typical of halogen compounds of the fatty series; that of benzyl chloride, of aromatic compounds containing halogen in the side chain; and that of brombenzene, of aromatic compounds having halogen attached to an aromatic nucleus. Some halogen compounds of the latter class, especially those containing also a nitro group, are decomposed by potassium hydroxide and give the reaction with silver nitrate.

Reaction Distinguishing Saturated and Aromatic Hydrocarbons and Their Halogen Derivatives from Other Compounds.

15. Add gradually, shaking constantly and keeping the mixture cool, 4 cc. of concentrated sulphuric

acid to 2 cc. of (*a*) toluene, (*b*) ethyl bromide, (*c*) phenol, and (*d*) ethyl acetate.

The behavior with cold sulphuric acid will generally distinguish saturated and aromatic hydrocarbons and their halogen derivatives from other compounds, most of which are either soluble in the acid or are destroyed by it. Among these other compounds there are, however, many which are unacted upon by sulphuric acid, but these exceptions are met with mostly among the acids and nitrogen compounds. The test is therefore especially useful in distinguishing hydrocarbons and their halogen derivatives from alcohols, phenols, ethers, and esters.

Reactions of Compounds Containing the Hydroxyl Group.

16. Add small pieces of sodium to 3 cc. of absolute alcohol, in a test-tube, as long as it dissolves. The sodium should be added fast enough to keep the solution hot without causing it to boil violently. Finally, cool the solution.

Substances to which this test is to be applied must first be thoroughly dried, if water is present. Solid or viscous substances must be dissolved in anhydrous ether or some other indifferent solvent. If the effervescence is only slight, the test must be tried as described in Experiment 10, in order to form an idea of the amount of gas evolved, and thus distinguish a slow action on a hydroxyl compound from that due to an impurity.

Besides hydroxyl compounds, some aldehydes, ketones, esters, and amides evolve hydrogen ; and the halogen compounds of the lower hydrocarbons of the fatty series give off gaseous hydrocarbons. On the other hand, a few hydroxyl compounds (for example, resorcin, and salicylic acid) fail to give evidence of a reaction with sodium.

Reactions of Alcohols and Phenols.

17. Add gradually 2 cc. of amyl alcohol to 4 cc. of concentrated sulphuric acid in a small test-tube, shak-

ing constantly and keeping the mixture cool. Allow it to stand two or three minutes, and then pour it into a test-tube containing about 12 cc. of water.

Repeat the experiment, using phenol in place of the amyl alcohol.

In the case of the higher fatty alcohols a layer consisting of the original alcohol or some insoluble reaction-product may separate out on the dilution of the sulphuric acid. Compare Experiment 32.

If the substance to be tested is soluble in water, it is not possible to determine in this simple manner whether or not it combines with the sulphuric acid. In that case the method illustrated by the following experiment must be employed.

18. Mix 2 cc. of strong sulphuric acid with 5 cc. of alcohol. After five minutes pour the mixture into 100 cc. of water, heat to boiling, and add barium carbonate until the liquid is neutral. Filter hot. Add dilute sulphuric acid to one-half of the filtrate. Evaporate the other half to dryness and ignite the residue.

Of the alcohols, only the primary ones of the fatty series give the reactions observed in this experiment. Phenols and some other aromatic compounds, however, give apparently the same result, owing to the formation of soluble sulphonic acids and soluble barium sulphonates

19. Add 2 cc. of acetyl chloride to (*a*) 1 cc. of ethyl alcohol and (*b*) 1 gram of phenol, and add the mixtures to 5 cc. of water. Use great caution, as the reactions with acetyl chloride are sometimes very violent.

Reactions of Alcohols.

20. Test the solubility of ethyl alcohol and of amyl alcohol in water and dilute sodium hydroxide solutions.

All monoatomic alcohols containing less that four atoms of carbon and almost all polyatomic alcohols are readily soluble in water; other alcohols are insoluble or difficultly soluble.

21. Place in a small flask 2 cc. of alcohol, 50 cc. of sodium hydroxide solution (1 : 10) and 5 cc. of benzoyl chloride. Shake until the odor of benzoyl chloride has disappeared.

Repeat the experiment, omitting the alcohol.

The odor observed in this experiment is a characteristic and delicate test for the lower monoatomic alcohols of the fatty series. Hydroxyl compounds in general, with the exception of acids, undergo a similar reaction; but the products do not possess the same characteristic odor.

Reactions of Phenols.

22. Test the solubility of phenol in water, in sodium carbonate solution, and in sodium hydroxide solution by adding the solvents little by little to 1–2 grams of the substance. Test the solubility of resorcin in water. Test the reaction of the aqueous solutions with alkaline phenolphthalein solution or with blue litmus paper.

23. Add a few drops of ferric chloride solution to solutions of phenol, of pyrocatechin, and of resorcin.

This test is applicable to neutral solutions only. In order that it may be regarded as indicating the presence of a phenol, a *strong coloration* must be obtained; for most hydroxyl derivatives give a faint yellow coloration. The most important phenols that fail to give this reaction are α-naphthol, the nitrophenols, and meta and para oxyacids. On the other hand, many aromatic amines give similar colorations; and oxyacids of the fatty series give a strong yellow coloration (compare Experiment 30).

24. Heat together in dry test-tubes for one or two minutes in an oil-bath at a temperature of 150°, 0.2 gram phthalic anhydride and a somewhat smaller quantity of phenol, α-naphthol, resorcin, and pyrocatechin, the mixtures being first moistened (not covered) with a

few drops of concentrated sulphuric acid. Treat the fused mass with 10 cc. of cold water, and add sodium hydroxide solution *very gradually* until no further change occurs. Dilute portions of the faintly alkaline solutions, and view them obliquely from above by reflected light.

25. Add bromine water to 5 cc. of phenol solution until the liquid assumes a permanent yellow color.

This reaction is a very delicate one for most phenols, but there are a few exceptions. Moreover, many aromatic amines also give a precipitate with bromine water.

Reactions of Organic Acids.

26. Test the solubility in water of benzoic acid and oxalic acid.

Nearly all acids containing more than six carbon atoms, except the aromatic sulphonic acids, are insoluble or very difficultly soluble in cold water. On the other hand, nearly all of the acids commonly met with containing a smaller number of carbon atoms are soluble.

27. To about 0.2 gram of benzoic acid add, in portions of 1 cc. at a time, a one per cent. solution of sodium hydroxide strongly colored by the addition of a little phenolphthalein solution.

In order to distinguish between considerable amounts and accidental traces of acids, the test is made in this way, so as to determine roughly the quantity of alkali required for the neutralization.

Some esters are so readily saponified that they cause, when tested as here described, a rapid decolorization of the solutions; but the action is never instantaneous, as is the case with most acids.

28. Treat 1 gram of benzoic acid with 5 cc. of water; add sodium carbonate solution, at first in small

quantity, and finally in slight excess; then acidify with hydrochloric acid.

29. Add 20 cc. of sodium formate solution (1 : 5) to 0.5 gram (weighed approximately) of the following acids in the state of *fine powder:* Benzoic, salicylic, phthalic, cinnamic.

All these acids are nearly insoluble in water. The experiment determines roughly the strength of the various acids as compared with formic acid. Those stronger than formic acid displace it and go into solution; those weaker do not. The strength of acids depends on their composition and *structure.* Of the aromatic acids, the sulphonic acids and the derivatives of benzoic acid and its homologues containing one or more nitro groups, or two or more halogens, or one halogen, hydroxyl or carboxyl group in the *ortho* position to the carboxyl group, are stronger than formic acid. Acids containing none of the mentioned "negative" groups, or containing one halogen in the *meta* or *para* position, or one or more hydroxyl groups in the meta or para position, are weaker than formic acid. (For a detailed list of the strengths or "affinity constants" of various acids see the Zeitschrift für physikalische Chemie, **3**, 418.)

Reaction of a-Oxy-acids.

30. Dissolve 0.1 gram of tartaric acid in 50 cc. of cold water, in a porcelain dish, and add two drops of a 10 per cent. ferric chloride solution.

Repeat the experiment, using sugar in place of tartaric acid.

As is illustrated by the latter part of this experiment, hydroxyl compounds in general give a slight coloration; but the color produced by the α-oxy-acids is very much stronger at the same concentration. It is, moreover, always a pure yellow.

Reactions of Ethers and Esters.

31. Add 1 cc. of ethyl ether first to 5 cc. of water, and then to 5 cc. of dilute sodium hydroxide solution.

Repeat the experiment, using amyl acetate in place of ethyl ether.

32. Repeat Experiment 17, using first ethyl ether and then amyl acetate in place of amyl alcohol.

Reactions of Compound Ethers or Esters.

33. Boil vigorously over a small free flame 5 cc. of ethyl benzoate with 40 cc. of potassium hydroxide solution (1 : 2) in a 200 cc. long-necked, round-bottomed (Kjeldahl) flask provided with a long return cooler of wide bore, until the odor of the ester disappears. Acidify half the solution with an excess of hydrochloric acid. Dilute the remainder with water to 100 cc., add 5 cc. of benzoyl chloride, and shake till its odor has disappeared, as in Experiment 21.

Since the ease of saponification varies greatly with the nature of the ester, the boiling should be continued until complete solution takes place, or until the ethereal odor disappears.

If the alcohol of the ester is insoluble, and if the acid of it is soluble in water, evidently the ester would not be detected by the method illustrated by the above experiment (except, perhaps, by the disappearance of its odor). In case, therefore, the above test gives a negative or indecisive result, proceed as in the following experiment.

34. Dilute about 25 cc. of (1 : 2) potassium hydroxide solution with a nearly equal volume of water. Introduce into a long-necked, round-bottomed flask of 200 cc. capacity 10 cc. of this solution by means of a pipette. Add to it about 5 cc. of amyl acetate. Connect the flask in an inclined position with a return cooler, and boil vigorously for twenty minutes. Rinse off the condenser and stopper into the flask, dilute to about 100 cc., add a drop or two of phenolphthalein solution, and titrate with hydrochloric acid

(one part acid of 1.12 sp. gr. to five parts of water) added by means of a graduated pipette. Titrate in the same way 10 cc. of the original (1 : 4) potassium hydroxide solution.

In case of unknown substances, if an appreciable amount of acid is found to be present by the test described in Experiment 27, it must first be removed by washing the substance with sodium carbonate solution, and then with water.

Aromatic aldehydes are also converted by potassium hydroxide into alcohols and acids. Moreover, amides, nitriles, some carbohydrates, and a few ketones are decomposed with formation of acids which combine with the potash.

Reactions of Acid Chlorides.

35. Add a *few* drops of water to 1 cc. of acetyl chloride.

It is generally necessary to heat acid chlorides in order to produce this decomposition.

Reactions Common to Aldehydes and Ketones.

36. Test the solubility of benzaldehyde in water and in dilute sodium hydroxide solution.

The lower aldehydes and ketones of the fatty series are, however, readily soluble in all these solvents. Acetaldehyde is converted by alkalies, especially on heating, into aldehyde-resin, a brown amorphous substance. In regard to aromatic aldehydes, see the note to Experiment 34.

Cold concentrated sulphuric acid either dissolves or destroys aldehydes and ketones.

37. Shake together for two or three minutes 3 cc. of acetone and 5 cc. of a saturated solution of sodium acid sulphite. If necessary, set aside and cool.

This reaction, while very characteristic, is not particularly delicate. Ketones give it only when they contain the group $CH_3.CO$. Solid substances should be dissolved in a very little

ether. In applying the reaction to unknown substances, always test the reagent first with a portion of acetone.

38. To 5 cc. of aldehyde solution add an equal volume of sodium acetate solution and a few drops of a solution of phenylhydrazine hydrochloride.

This test is, as a rule, most satisfactorily applied in aqueous solution, most aldehydes and ketones being sufficiently soluble in water for the purpose. In some cases, however, it is necessary to use some other solvent than water; but in that case a negative result is not decisive, since the hydrazone formed may be soluble.

Reactions of Aldehydes (not Ketones).

39. Mix in a test-tube previously cleaned with hot sodium hydroxide solution 1 cc. of ammoniacal silver nitrate solution and 1 cc. of ten per cent. sodium hydroxide solution. Shake the mixture about in the tube, and then allow two or three drops of aldehyde solution to flow slowly down the moistened glass surface. *Do not warm the mixture.*

This test is known as the Tollen's reaction for aldehydes. The ammoniacal silver solution contains one part of silver nitrate dissolved in ten parts of ammonia water of sp. gr. 0.923. When mixed with sodium hydroxide, a dangerously explosive precipitate is apt to form on heating or on long standing.

Some compounds other than aldehydes, especially di-atomic and tri-atomic phenols and amidophenols, reduce ammoniacal silver solution.

40. Pour two or three drops of aldehyde solution into 5 cc. of cold fuchsine-aldehyde-reagent.

This aldehyde-reagent is prepared by dissolving one part of a rosaniline salt in one thousand parts of water, and then adding enough of a strong sulphurous acid solution to destroy the red color on standing. An excess of sulphurous acid does not interfere with the reaction. Some ketones when added to the reagent in relatively large quantity give the same reaction as aldehydes; but the change occurs much more slowly.

Reaction for Carbohydrates.

41. Add to pieces of sugar, starch, and filter paper not larger than a mustard seed 0.5 cc. of water, two drops of a 20 per cent. alcoholic solution of α-naphthol, and 2 cc. of concentrated sulphuric acid. Dilute with water and add a slight excess of potassium hydroxide solution.

The composition of the compound formed is unknown.

The tests for aldehydes and ketones described in the preceding experiments are, as a rule, not applicable to carbohydrates.

Reactions of Aromatic Nitro-Compounds.

42. Add 1 cc. of nitrobenzene to 5 cc. of water, to 5 cc. of dilute hydrochloric acid, and to 5 cc. of dilute sodium hydroxide solution.

Nitro-compounds, particularly those containing two or more nitro groups, color sodium hydroxide solution deep red or yellow.

43. Repeat Experiment 17, using nitrobenzene in place of the amyl alcohol.

Trinitro-compounds and many other nitro-compounds containing other substituted groups require heat for their solution in sulphuric acid.

44. To 1 cc. of nitrobenzene, in a wide test-tube, add 2–3 grams of granulated tin; and then add, in several small portions, 5 cc. of hydrochloric acid of 1.2 sp. gr., with constant shaking. The temperature and the addition of the acid should be regulated so as to secure a moderate reaction. In order to complete it, gentle heat and the addition of more tin or acid may be necessary. Pour the clear solution into a beaker, dilute with 10 cc. of water, and add potassium hydroxide solution (1 : 2), until the solid precipitate formed at first has for the most part redissolved.

Reactions of Amines.

45. Test the solubility of aniline in water and dilute hydrochloric acid (1 : 10); and then make the acid solution alkaline with potassium hydroxide.

Aromatic amines containing negative substituted groups (for example, dinitraniline) or two or more aromatic radicals (for example, triphenylamine) often may not dissolve in hydrochloric acid of this strength, owing to the decomposition of their salts by water.

46. Dissolve a little aniline in the least possible amount of hydrochloric acid, and add a few drops of this solution to 1 cc. of hydrochloroplatinic acid.

The platinum salts of many amines are soluble, and therefore do not precipitate under these conditions.

47. Add acetyl chloride cautiously, drop by drop, to 1 cc. of aniline, in a small flask, until there is no longer any apparent action. Add carefully 25 cc. of water to the product.

Tertiary amines and most amines containing negative groups fail to react with acetyl chloride in the cold.

Compare Experiment 19.

48. Add gradually an excess of bromine water to a drop of aniline suspended in 2 cc. of water.

Compare Experiment 25.

Reactions Distinguishing Amines of Different Types.

49. Warm under a hood one or two drops of aniline, to which a few drops of chloroform have been added, with 1 or 2 cc. of alcoholic potassium hydroxide solution.

Only primary amines give rise to the odor observed in this experiment. The test is so delicate, however, that it is difficult

to distinguish by means of it a minute trace of a primary amine from a considerable amount. The following experiment enables us to do this with certainty.

50. Add to 1 gram of aniline in a test-tube 5 cc. of water and 5 cc. of hydrochloric acid (sp. gr. 1.12). Cool the solution in ice water, and add to it gradually, keeping it well cooled, about 3 cc. of a sodium nitrite solution (1 : 3), until, after shaking, the mixture smells distinctly of nitrous acid. Now insert in the test-tube a stopper with a delivery tube, and warm the mixture gently, collecting the gas evolved in an inverted 200 cc. bottle filled with a saturated ferrous sulphate solution; shake the bottle until no further absorption of gas takes place.

Repeat the experiment, using first methylaniline, and then dimethylaniline, in place of aniline.

Amides are also decomposed with evolution of gas, but as a rule less readily than amines. The reaction is, indeed, almost universally applicable for the detection of the NH_2 group in amines appreciably soluble in dilute hydrochloric acid, even substitution-products like sulphanilic acid, undergoing the reaction readily.

51. Add very cautiously 1 cc. of acetyl chloride first to 1 cc. of methylaniline, and then to 1 cc. of dimethylaniline.

Compare the results with those of Experiment 47.

52. Add to about 0.5 gram of aniline 50 cc. of potassium hydroxide (1 : 4) and 2 grams of benzenesulphonyl chloride, shake for two or three minutes, and then warm till the odor of the chloride disappears. Acidify the solution with hydrochloric acid.

Repeat the experiment, using first methylaniline, and then dimethylaniline, in place of the aniline. In

these two cases filter before acidifying the solution, and test the solubility of the precipitate on the filter in dilute hydrochloric acid.

Reactions of Amides and Nitriles.

53. Test the solubility of urea and of acetanilide in water, and that of the latter substance in dilute hydrochloric acid (1 : 10).

54. Boil 1 gram of urea with 5 cc. of potassium hydroxide solution for two or three minutes. Acidify the solution with sulphuric acid.

Repeat the experiment, using acetanilide in the place of urea.

Ammonium salts and those of amines are readily decomposed by potassium hydroxide *in the cold.* Some amides (for example, urea) are also *slowly* decomposed in the cold, but there is little danger of confounding them with ammonium salts.

Nitriles, like amides, are decomposed by boiling with alkalies; but the former may usually be distinguished from the latter by their greater volatility.

Reaction of Aromatic Sulphonic Acids.

55. Fuse 1 gram of sodium hydroxide in a small nickel or porcelain crucible heated on an iron plate. Add to the fused mass about 0.5 gram of sodium benzenesulphonate; and continue the heating for about five minutes, with occasional stirring, regulating the temperature so that the mass remains liquid, and so that it does not char. After cooling, dissolve the product in water, acidify with dilute hydrochloric acid, filter, and add bromine water.

PART II.

EXPERIMENTS ILLUSTRATING THE METHODS OF DETECTION OF NITROGEN, SULPHUR, AND HALOGENS IN ORGANIC COMPOUNDS.

Subject portions of aniline, sulphurea, chloroform, and bromnitrobenzene, each separately, to the following treatment:

Preparation of the Solution. — Prepare an ignition-tube about four inches in length from a piece of hard glass combustion-tubing. Warm the closed end by passing it rapidly back and forth through a flame. Then support the tube in a vertical position by a clamp, and drop in a piece of pure sodium as large as a pea. Place a small flame directly beneath the ignition-tube, and quickly heat the bottom of it to redness. As soon as the vapor of the melted sodium forms a layer half an inch in height, allow about five drops of the substance if a liquid, or an equivalent quantity of fragments if a solid, to fall at intervals of one or two seconds directly upon the red-hot bottom of the tube without touching its side walls. When the tube has become cold remove any excess of metallic sodium by adding a very little alcohol. Next, add very cautiously a little distilled water, stir well with a glass rod, rinse the contents of the ignition-tube into a test-tube, bring to a boil, and filter. The filtrate should be nearly colorless and measure about 15 cc. Separate portions of this filtrate are to be used in the following tests:

Tests for Sulphur. — To 1 cc. of the prepared solution add two or three drops of a dilute sodium nitroprusside solution.

To 1 cc. add two or three drops of a solution of lead acetate made strongly alkaline with sodium hydroxide.

Only alkaline sulphide solutions give the reaction with sodium nitroprusside.

Test for Nitrogen. — Boil gently 2 cc. of the prepared solution for two minutes with five drops of sodium hydroxide solution, five drops of ferrous sulphate solution, and one drop of ferric chloride solution. Then add just enough dilute hydrochloric acid to dissolve the precipitated ferrous and ferric hydroxides, and, if no precipitate appears at once, allow the mixture to stand.

Test for Nitrogen and Sulphur when Present Together. — Faintly acidify 1 cc. of the prepared solution with hydrochloric acid and add two or three drops of ferric chloride solution.

When this test gives a negative result, it does not prove conclusively the absence of sulphur and nitrogen, or of either of them; for the sodium sulphocyanate is decomposed by an excess of sodium into sodium sulphide and cyanide. It is, nevertheless, advisable always to try this test when the previous tests have shown the presence of either nitrogen or sulphur, since otherwise one of these elements may be overlooked.

Tests for Halogens when Sulphur and Nitrogen are Both Absent. — Acidify 1 cc. of the prepared solution with dilute nitric acid, and add a few drops of silver nitrate solution. If a precipitate forms, acidify a larger portion with hydrochloric acid, add a few drops of carbon bisulphide, and then chlorine water little by

little, continuing the addition, if iodine is present, until the violet color disappears.

Test for Halogens when Either Sulphur or Nitrogen is Present. — Acidify the remainder of the prepared solution with dilute nitric acid, and boil for five minutes in an open vessel to expel hydrogen sulphide and hydrocyanic acid. Filter, if necessary, and subject the solution to the tests described in the preceding paragraph.

It is to be remembered that, if sulphocyanate is present in the solution, a precipitate will be obtained with silver nitrate, whether halogens are present or not; but the presence of sulphocyanate will not affect the tests for bromine and iodine with chlorine water and carbon bisulphide. For the methods of detecting chlorine when the other halogens or sulphocyanic acid is present, Fresenius' Qualitative Analysis may be consulted.